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A multifunctional fluorescent probe for highly selective detection of

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Abstract: A multifunctional luminescent material (**BC-B**) was synthesized, which exhibits aggregation-induced emission (AIE) enhancement property in high water fraction. The AIE shows a significant impact on the intramolecular charge transfer (ICT) process by controlling intramolecular motion. The above result is demonstrated by density functional theory (DFT) calculations and single-crystal X-ray diffraction. To decrease the influence of AIE on ICT, the probe **BC-B** is exploited as turn-on fluorescent probe for hydrazine (N₂H₄) in DMSO/PBS buffer (6/4, v/v) and displays high sensitivity and selectivity. Besides, the fluorescence emission shows a good linear response ($\mathbb{R}^2 = 0.9960$) in the range of 0 - 35 µM with the low detection limit of 1.29 ppb, which is significantly below the acceptable limit for hydrazine (10 ppb) set by the USEPA.

Keywords: Aggregation induced emission; Intramolecular charge transfer; Hydrazine (N₂H₄); Density functional theory; Fluorescent probe.

1. Introduction

Fluorescent probes have become more and more effective for monitoring various biological and environment-specific analytes with the advantages of easy operation, high visibility, high sensitivity and good selectivity [1, 2]. Over the past few decades, the encouraging progress of fluorescent probe was made [3, 4]. The primary strategy relies on fluorescent changes before and after interaction with target analytes by one or more frequently used sensing such as aggregation-induced emission (AIE) [5, mechanisms, 6]. intramolecular charge transfer (ICT) [7], photo-induced electron transfer (PET) [8, 9], etc. Among those, the ICT based molecules are mainly consist of an electron donating (D) and an electron acceptor (A) group with extended π -conjugated spacer. The push-pull structure leads to an efficient ICT from donor to acceptor part and generation of a molecular dipole. The properties of dipolar chromospheres can be easily adjusted by modification of the donor-acceptor pairs [10-13]. The degrees of charge transfer in the ground and excited-state partially depend on the ambient medium as polarity of solution, testing temperature and nature of the electron donating and accepting substituents. Unfortunately, these factors mentioned above can result in an increase false probability [14]. The fluorescent probe is usually influenced by weak interactions such as van der Waals, $\pi \cdots \pi$ stacking, hydrophobic, and hydrogen-bonding interactions, which may cause the different properties of aggregation state and individual molecule [15]. Notably, the π -conjugated molecules are always resulting fluorescence quenched in aggregated state due to the tight π - π stacking and non-radiative decay [16]. Most conventional photo-active organic compounds with aggregation-caused quenching (ACQ) exhibit strong emission in dilute solution but weak luminescence in the solid-state or in aqueous solution. Some AIE organic molecules have the opposite results with ACQ. The AIE provides an effective solution to the ACQ problem by restriction of intramolecular motions [17, 18]. As a result, the molecules of AIE mechanism or AIE plus others have been rapidly developed in optoelectronic

devices, fluorescent sensors, and stimuli-responsive materials [19-22]. However, few compounds concurrently exhibit AIE and ICT properties and the interaction of which is rarely discussed in theory.

Hydrazine (N₂H₄) is widely applied in various industry areas for its unique properties, including a strong reductant, nucleophilicity and high heat of combustion [23, 24]. But it may lead to serious environmental pollution problems and damage to organs and central nervous system because of high toxicity [25]. Therefore, the development of reliable, sensitive, selective and accurate detection methods of hydrazine is an urgent requirement for human health and safety. Up to now, exploiting strong nucleophilicity and different recognizing moieties, the research has acquired great achievements in detection for N₂H₄ [26-30]. But the overall point of view, there are still some defects which can limit their application. For example, some probes based on aldehyde or ester as recognition sites were usually interfered by other competitive amines and related species [31, 32]. Few probes were used to detect N₂H₄ at high water fraction and low pH value [33].

The 4-bromo butyrate-based probes were developed for the hydrazine detection by a substitution-cyclization-elimination reaction, as these probes usually have excellent specificity [34- 37]. In this work, a novel luminescent material **BC-B** based on ICT mechanism was designed and synthesized by grafting 4-bromo butyrate on coumarin moiety (Scheme 1). The **BC-B** displayed AIE enhancement characteristic. The intermolecular interactions (e.g. $\pi \cdots \pi$ stacking and intermolecular hydrogen bonds) impacted on the ICT process, which was confirmed by the single-crystal X-ray diffraction and DFT calculation. Furthermore, it did not response to N₂H₄ in aggregation state. When the influence of AIE on ICT was lessened, it was successfully used to detect hydrazine with high selectivity and sensitivity in DMSO/PBS buffer (6/4, v/v, pH 7.4, 10 mM).

2. Experimental

2.1. Materials and instruments

The coumarin fluorescent dye (BC) was prepared by a modified procedure according to the literature [38]. Dimethylsulfoxide (DMSO) was chromatographic pure. Other chemical reagents and solvents chemicals for synthesis were provided by commercial suppliers and used as received without further purification unless otherwise stated. Ultrapure water was purified from Millipore. ¹H NMR and ¹³C NMR data analyses were performed with a Varian Mercury plus-600 instrument unless otherwise specified. CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard were employed. HRMS data was carried out on a Thermo Scientific Q Exactive. The UV-Vis and Fluorescence spectra were collected on a a HORIBA FluoroMax-4. TU-1901 spectrophotometer and Solid-phase fluorescence was measured using film. The fluorescent intensity was adjusted using appropriate filters. The product of the reaction between BC-B and N₂H₄ was purified, and the solid IR spectrum was recorded on NEXUS as KBr pellets. An X-ray single-crystal diffractometer was collected on a Bruker APEX-II CCD. The SEM measurements were obtained on an Ultra Plus scanning electron microscope. The pH measurements were performed on a PHS-3C pH meter. Melting points were measured with an XT-4 apparatus. TLC analyses and the applicability test of BC-B were conducted on silica gel GF254 plates. Column chromatography was generally performed on silica gel (200-300 mesh).

2.2. Preparation of sample solutions

The stock solution of **BC-B** was prepared in DMSO (2 mM). To test the AIE property, the stock solutions (50 μ L) were transferred to 10 mL volumetric flasks. After corresponding amount of DMSO and pure water were added to afford 10 μ M solutions with different water fraction and then measured its absorption and fluorescence spectra. For the other spectral measurement, 3 mL DMSO/PBS buffer (6/4, v/v, pH 7.4, 10 mM) solvent was added into a quartz cuvette (1 cm×1 cm), followed by the addition of 15 μ L probe stock solution to give the sample solution with probe concentration of 10 μ M. After a certain amount of N₂H₄ stock solution (10 mM) was added in titration experiments, the fluorescence spectra were recorded.

For the selectivity experiment, 10 mM relevant analytes stock solutions were prepared in water.



Scheme 1. Design and synthesis of probe BC-B

2.3. Synthesis of luminescent material **BC-B**

The solution of compound 4-dimethylaminopyridine (DMAP, 4 mg, 0.03 mmol), 1-ethyl-3-(3-(dimethylamino)propyl) carbodiimide hydrochloride (EDC·HCl, 100mg, 0.53 mmol) and 4-bromobutyric acid (71 mg, 0.36 mmol) in anhydrous dichloromethane (50 mL) under N₂ atmosphere was stirred for 30 min, then the compound **BC** (72 mg, 0.2 mmol) was added. The mixture was constantly stirred overnight at room temperature. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography (CH₂Cl₂ /CH₃OH from 50/1 to 10/1, v/v) to obtain probe **BC-B** (66 mg, 65%). m.p. 161 ~ 163 \Box . ¹H NMR (600 MHz, CDCl₃) δ 8.52 (s, 1H), 8.10 (d, *J* = 15.7 Hz, 1H), 7.77 (d, J = 15.7 Hz, 1H), 7.67 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.9 Hz, 1H), 7.11 (d, J = 10.0 Hz)8.5 Hz, 2H), 6.60 (dd, J = 9.0, 2.3 Hz, 1H), 6.46 (s, 1H), 3.53 (t, J = 6.4 Hz, 2H), 3.43 (q, J = 7.1 Hz, 4H), 2.77 (t, J = 7.2 Hz, 2H), 2.28 (m, 2H), 1.22 (t, J = 7.1 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 186.2, 170.7, 160.8, 158.7, 153.0, 151.9, 148.7, 141.8, 133.2, 131.8, 129.77, 125.2, 121.9, 116.5, 109.9, 108.6, 96.6, 45.1, 32.6, 32.4, 27.5, 12.5. HRMS calcd for C₂₆H₂₇BrNO₅ [M+H]⁺: 512.1067 found: 512.1061, 514.1037.

3. Results and discussion

3.1. The AIE properties of **BC-B**

The UV-Vis absorption and fluorescent emission spectra of BC-B were

systematically investigated in various solvents (Fig. 1). The main absorption bands located at 300-360nm and 360-500nm (Table S1) belong to π - π * transitions and intramolecular charge transfer (ICT). With the increasing of solvent polarity from hexane to DMSO, the absorption spectra of **BC-B** demonstrated a red-shift about 29 nm, which illustrated that the BC-B contained polar characteristic in the ground state. The fluorescent emission displayed a large range of red-shift (95 nm) with changing the polarity from Hexane to MeCN, demonstrating an intense ICT process in the excited-state. With the increase of polarity from CH_2Cl_2 to CH_3OH , the emission intensity was gradually weakened and even invisible. It was possible because strong polarity solvents destroyed the weak interactions which caused TICT phenomena [39]. Such dramatic changes of emission displayed that the BC-B had a remarkable solvatochromic effect. Further research was launched to the relationship between the solvent polarity parameter (Δv) and the Stokes shift (Δf) . The Stokes shift was gradually increased with enhancement of solvent polarity. The Lippert-Mataga equations (Fig. S1) showed a linear relationship. Which further suggested the BC-B was strong dipolar characteristic with remarkable solvatochromic effect. The UV-Vis absorption and fluorescent emission spectra of BC were investigated (Fig. S2). The results showed that BC also had dipolar characteristic and solvatochromic effect. (Table S2 and Fig. S3).



Fig. 1 (a) The UV-Vis spectra and (b) fluorescent intensity of BC-B (10 μ M) in different solvents ($\lambda_{ex} = 393$ nm, slit ex/ em = 2/3 nm).

To investigate the AIE performance of BC-B, the UV-Vis and fluorescent emission spectra were carried out in H₂O/DMSO mixtures as shown in Fig. 2a. The absorption bands showed that there were little changes at 323 nm and 465 nm as the water fraction (f_w) below 40 vol%. The **BC-B** mainly existed in non-aggregated state. With the increasing of f_w from 60 vol% to 90 vol%, the absorbance bands disappeared at 465 nm, and new blue-shift absorption peaks were observed at 423 nm, where the BC-B mainly existed as molecularly aggregation state. The blue-shift was due to the restriction of ICT process which caused the increase of π - π * transition energy in aggregation state. Then, fluorescence emission was discussed as shown in Fig. 2b. The **BC-B** showed a weak emission at 548 nm as the f_w was less than 20 vol%. The emission was nearly quenched from 20 vol% to 40 vol% because of TICT transition. The fluorescent intensity (λ em = 564 nm) was significantly enhanced with the increasing of f_w from 60 vol% to 80 vol%. The maximum emission intensity (f_w =80 vol%) was approximately 12.9-fold increase in comparison with f_w =40 vol% (Fig. S4). Meanwhile, as shown in Fig. S5, an intense red-shifted peak (λ em = 614 nm) could be observed in solid state, the Stokes shift (191 nm) of solid was larger than in pure water (146 nm). These properties indicate that the **BC-B** could be used as a typical AIE enhancement luminescent material. Moreover, the red-shift of emission peaks from solvent to solid state showed that the tighter the molecular packing was, the smaller HOMO - LUMO energy gap. However, as shown in Fig. 3 and Table S2, the maximum emissions (525 nm and 564 nm) of BC-B were not significant changes after the addition of 20 equiv N₂H₄ at high water fraction. These results showed the ICT process was probably restricted in aggregation state. The AIE performance of BC was also investigated, as shown in Fig. S6. The absorption intensity of **BC** suddenly decreased, and the fluorescence intensity was up to a minimum ($f_w=70$ vol%). Then it was increased to the maximum at 80vol%. All of these changes were like to BC-B

, but the changes of fluorescence intensity were small. The **BC** exhibited weak AIE enhancement property. The scanning electron microscope (SEM) was also exploited to investigate the formations of **BC-B** in solution ($f_w = 10$ vol%) (Fig. S7a) and aggregation state ($f_w = 80$ vol%) (Fig. S7b). The SEM images showed that the spherical aggregation morphology could be found by the self-assembly strategy in aggregation state.



Fig. 2 The UV-Vis spectra (a) and fluorescent intensity (b) of BC-B (10 μ M) in DMSO/H₂O mixtures with different water fractions. (insert: the fluorescent changes under 365 nm UV-light)



 $(\lambda_{ex} = 393 \text{ nm}, \text{ slit ex}/\text{ em} = 3/3 \text{ nm}).$

Fig. 3 Plots of maximum emission intensity (λ_{em} = 525 nm) of BC-B (10 μ M) (black) and BC-B upon addition 20 equiv N₂H₄ (red) in the DMSO/ H₂O mixtures with different fws. (λ_{ex} = 393 nm, slit ex/ em = 3/3 nm).

3.2. Molecular orbital calculations

In order to gain deep insights into AIE and ICT process, the theoretical calculations using density functional theory (DFT) and time-dependent DFT (TD-DFT) based on B3LYP/6-311G (d, p) level using the Gaussian 09

program were performed. The optimized geometry showed that the molecule of the series adopted a nearly planar structure as shown in Fig. S8. This structure was favorable to the aggregation of molecule. Almost all of electron cloud of HOMO was distributed in acryloylcoumarin moiety (Fig. 4), while the LUMO was transferred and evenly distributed in the aromatic ester group and acryloylcoumarin moiety with an energy gap of 3.02 eV. As showed in Table S3, the $S_0 \rightarrow S_1$ transition was a major contribution of HOMO-1 to LUMO (97.7 %) at 460 nm with oscillator strength (f = 1.066). This value was highly consistent with the experimental absorption wavelength (464 nm). The HOMO of BC mainly was located on the coumarin unit, whereas the LUMO was distributed throughout π -conjugated moiety. The $S_0 \rightarrow S_1$ transition for **BC** with the energy gap of 3.08 eV was a major contribution of HOMO-1 \rightarrow LUMO (96.8 %) at 452 nm with oscillator strength (f =1.200). Especially, the push-pull structure alteration led to the dipole moment which decreased from 14.18 (BC-B) to 7.97 (BC). The above results suggested that the probe **BC-B** was stronger **ICT** process than **BC** in solution, which also provided support for the experimental prediction of solvatochromic effect for BC-B and BC.



Fig. 4 Calculated electronic density contours and energy gaps of BC-B and BC.

3.3. Molecular and crystal structure

The AIE effect and bright solid-state fluorescence of BC-B trigger us to

elucidate their molecular conformation and arrangement in aggregation. Fortunately, the single-crystal of BC-B was obtained by slow evaporation from the solutions in dichloromethane/ether at room temperature. As shown in Fig. 5a, Fig. S10 and Table S4, the single crystal structure of BC-B contained various small dihedral angles and exhibited larger twisted conformation than optimized geometry structure, which confirmed that the intermolecular force of solid **BC-B** was more strength than that of its aqueous solution. Which also explained the red-shift of the solid emission. As shown in Fig. 5b and 5c, the asymmetric molecular conformations of head-to-head stacking were linked together to form 1D zigzag chain along a-axis by intermolecular $\pi \cdots \pi$ packing interactions (4.070 Å and 3.218 Å). The 1D chains were connected into a two-dimensional molecular by two types of intermolecular hydrogen bond with distances of 2.517 Å (C25-H25···O3) and 2.490 Å (C10-H10...O1). The overlap between electron-donating units and electron-withdrawing units formed dense packing conformations, which likely decreased the ICT process by controlling intramolecular motions.



Fig. 5 (a) X-ray crystal structure of **BC-B**. (b) intermolecular π - π interaction in the 1D zigzag chain along a-axis. (c) intermolecular hydrogen bonds in the 1D zigzag chain.

3.4. Spectral response of the probe to hydrazine

Because of these, the probe BC-B can be used for the detection of N_2H_4

if the influence of AIE on ICT is lessened. Firstly, the time-dependent fluorescent responses of **BC-B** in the absence and presence of N_2H_4 were studied. As shown in Fig. S11, in the absence of N_2H_4 , the fluorescent emission intensity of **BC-B** remained no variation in 10 min, clearly indicating its good photostability. After 20 equiv N_2H_4 was added into above solution, a significant enhancement emission was observed within a few minutes. The stable plateau emerged at 25 min later. Secondly, the pH-dependent experiments showed (Fig. S12) that the fluorescent intensity was nearly constant in the pH range of 3 - 12. After the addition 20 equiv N_2H_4 into **BC-B**, the fluorescent intensity exhibited remarkable enhancement in the pH range of 5.0 - 10.0. Therefore the probe **BC-B** could be used to detect hydrazine in a wide pH value range.



Fig. 6 (a) Fluorescent response of probe **BC-B** (10 μ M) to 20 equiv various analytes; (b) The selectivity of fluorescent ratio (F/F₀) response to various amines (n-butyl amine, ethylenediamine, methylamine, hydroxyl amine, urea, thiourea, ammonia, Cys, GSH, Hcy, Gly, Glu, hydrazine) in DMSO/PBS buffer (6/4, v/v, pH 7.4, 10 mM) (λ ex = 393

nm, $\lambda em = 525$ nm, slit ex/ em = 3/3 nm).

The selectivity of probe **BC-B** was examined, as shown in Fig. 6 and Fig. S13, no significant fluorescent changes were observed upon **BC-B** exposure with various analytes, except hydroxyl amine (blue line) resulted in a slight enhancement. In contrast, when N_2H_4 (red line) was added, the fluorescent intensity of **BC-B** at 525 nm was significantly increased

approximately 10.8-fold. Moreover, most of the analytes showed little impact on N_2H_4 detection. These results illustrated that the **BC-B** was highly selective for N_2H_4 over most of analytes.

Furthermore, fluorescent titration experiments were employed for researching the sensitivity of **BC-B** toward N₂H₄. As shown in Fig. 7, the fluorescent intensity was increased with the increasing concentration of N₂H₄. Simultaneously, the color of **BC-B** was changed from colorless to blue-green under 365 nm UV-light (inset of Fig. 7a). This remarkable color change indicates that probe **BC-B** can detect N₂H₄ by the naked eye. The fluorescent intensity showed a good linear response (R² = 0.9960) to N₂H₄ in a wide concentration range at 0-35 μ M. The detection limit was determined to be 1.29 ppb based on the general 3 σ /k method, and the value was much lower than 10 ppb suggested by EPA [40, 41], which was also equivalent or superior to previously reported N₂H₄ probes (Table. S5).



Fig. 7 (a) Fluorescent intensity of **BC-B** (10 μ M) with different concentrations of N₂H₄ (0–70 μ M) in DMSO/PBS buffer. Insets: the fluorescent change in the absence and presence of N₂H₄ under 365 nm UV-light; (b) The linear correlation between the fluorescence intensity and the concentration of N₂H₄ in the range of 0 - 35 μ M (λ ex = 393 nm, λ em= 525 nm, slit ex/ em= 3/3 nm).

After the **BC-B** was reacted with N_2H_4 , as shown in Fig. S14, a new peak was observed in IR spectra at 3248 cm⁻¹ (–OH). The disappearance of 1699 cm⁻¹ (-C = O) and 2927 cm⁻¹ (-CH₂) indicated that 4-bromobutyric was

eliminated. The HRMS (Fig. S15) exhibited the expected peak at 364.1538 corresponding to the **BC** ($[M+H]^+$ calcd 364.1543). Therefore, the detection mechanism toward hydrazine could be undergone a substitution- cyclization-elimination process as shown in Scheme S1 [42].

3.5. Detection of gaseous hydrazine

To check the applicability of **BC-B** as an optically efficient probe for N_2H_4 . A solution of BC-B (100 μ M) in DMSO/H₂O (6/4, v/v) was prepared, and then the letters "NWNU" were written on a glass TLC plate with a brush. The TLC plates were dried to slightly dry before exposing to hydrazine vapor. Next it was placed on a cushion in the sealed bottle containing vapors of N_2H_4 for 30 min. Particularly, this was done in the concentrated solution of N_2H_4 which was poured into the sealed bottle before 2 hours. As shown in Fig. 8, TLC plates of **BC-B** showed an orange fluorescent and faint orange as exposing to vapors of N_2H_4 under the daylight. Under 365nm UV light, TLC plates of **BC-B** showed bright yellow fluorescent and blue-green after interaction with hydrazine vapor. These further supported that the **BC-B** could be used as potential AIE luminescent material and fluorescent probe for N_2H_4 both in solution and on surface of a TLC plate.



Fig. 8 Photographs of **BC-B** (100 μ M) in the sunlight (a) alone and (b) exposed to vapors of N₂H₄ for 30 min later. The visible color changes of **BC-B** (100 μ M) under 365 nm UV light (c) alone and (d) in the presence of hydrazine vapors. (e) The photograph of crystal **BC-B** under 365 nm UV-light.

4. Conclusions

In summary, a novel luminescent material BC-B was successfully designed and conveniently synthesized. The obtained BC-B was featured with the AIE and ICT characteristics. In aggregation state, it mainly exhibited AIE enhancement performance, which could be used as AIE enhancement luminescent material with excellent photostability and significant Stokes shift. However, the BC-B virtually showed no response to hydrazine in high water fraction. The single-crystal X-ray diffraction and DFT calculations investigation demonstrated that the AIE had considerable impact on ICT interaction: packing interactions process by weak $\pi \cdots \pi$ and hydrogen-bonding. As the influence of AIE on ICT was reduced, the BC-B was employed for turn-on detecting N₂H₄, which showed low detection limit (1.29 ppb), high sensitivity and selectivity. Additionally, this study provides a valuable theoretical tool for further design of probes and selection of detection methods.

Conflicts of interest

There are no conflicts to declare.

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Highlights:

- A novel fluorescent probe BC-B was synthesized and showed aggregation-induced emission (AIE) enhancement performance.
- The influences of the AIE on the ICT process were demonstrated by density functional theory (DFT) calculations and single-crystal X-ray diffraction.
- The probe BC-B was applied to turn-on detection of N₂H₄ with high sensitivity and selectivity by lessening the AIE influences on the ICT process.

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Conflicts of interest

There are no conflicts to declare.

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author statement:

I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. Furthermore, the publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out.

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